ELECTRONIC STRUCTURE AND BAND LINEUPS AT THE DIAMOND/BORON NITRIDE AND DIAMOND/NICKEL INTERFACES

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Using both Gaussian local-orbital and linearized augmented plane wave basis sets, we have carried out self-consistent local-density-functional calculations of the electronic structure and bonding characteristics of an ideal unrelaxed diamond/BN (110) interface, and of a series of ideal diamond/Ni (100) and (111) interfaces. Our results include predictions of the band line-ups across the interfaces (the valence and conduction band discontinuities) in the former case, and the Schottky barrier height in the latter case. The diamond/BN system is predicted to be a type-II system, while the calculated diamond/Ni Schottky barrier heights depend strongly on the coordination of Ni atoms at the interface.

1. Introduction

The last few years have demonstrated that diamond-structure carbon can be grown from the vapor phase at low pressure. Diamond has many desirable properties, such as a large band gap and stability at elevated temperatures, that make it enticing for high frequency, high power, and high temperature applications. Although diamond films capable of performing in opto-electronic applications have yet to be fabricated, advances have continued ever since the report by Mishima *et al.* [1] of operating p-n diodes made from cubic BN. In anticipation of success in the fabrication of device-grade heterojunctions, we have carried out a series of calculations of the electronic structure of interfaces between diamond and other materials. This follows the substantial related work that has been done on many other covalent semiconductors such as Si, GaAs, and Ge.

2. Interface Geometry and Computational Methods

Our initial investigations were of the diamond/BN (110) interface, a natural choice because the properties of BN are so similar to diamond and the lattice mismatch is small. For a prototype diamond/metal system we have chosen Ni for the metal, because of recent attempts (only marginally successful so far) to grow diamond films on Ni substrates [2,3,4]. The lattice mismatch in this case is also small (1.5%).

For the diamond/BN system the choice for the (110) interface geometry is clear, and is identical to that chosen for other diamond-structure/zincblende-structure interfaces such as Ge/GaAs [5]. A lattice constant of 6.78 a.u. was used, which lies midway between that of diamond and BN.

For the diamond/Ni (100) and (111) interfaces the choice of interface geometry is not so obvious. For each interface we have chosen two relative orientations for the Ni and diamond layers abutting the interface: (i) a positioning of the interface Ni layer, with respect to the interface C layer, that preserves four-fold (approximately tetrahedral) coordination of the C atoms at the interface, and (ii) an in-hollow placement of the Ni surface atoms with respect to the C surface atoms, resulting in the higher coordination more typical of metallic bonding. The diamond lattice constant of 6.74 a.u. was used, corresponding to epitaxial growth of Ni on diamond with neglect of lattice mismatch and strain. Of course, the C-Ni distance must be greater than the (very short) C-C distance in diamond, and for some of the interfaces this distance has been relaxed to minimize the calculated energy. Several superlattice sizes have been studied, with supercells containing up to five layers of Ni and twelve layers of C. Schottky barrier heights were calculated from C core-level shifts: by aligning the 1s level from the most bulk-like C atom (i.e. furthest from the interface) with the 1s level from a bulk diamond calculation, the diamond valence-band edge E_V can be precisely located relative to the Fermi level E_F of the diamond/Ni supercell, giving the barrier height as

$$\Phi_B = E_F - E_V. \quad (1)$$

For the calculations of the electronic structure we have taken the self-consistent local-density-functional

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approach, with the exchange-correlation functional given by Hedin and Lundqvist [6], so that once the geometry is given no further information (experimental or by way of parametrization) is used. Calculations have been carried out with the linearized augmented plane wave (LAPW) method, with details given in [7] and [8], and a Gaussian local-orbital method, described in [7] and [9].

3. Selected Results and Discussion

Diamond/BN (110) Interface

The results for the (110) diamond/BN interface have been presented previously [8], so we present only the most prominent results here. By performing calculations on superlattice cells of 1, 3, and 5 layers of each material, it was found that many local properties are similar to their bulk values already in the second layer from the interface. This reflects the close similarity of the bonding in the two materials: disruptions in bonding, leading to a perturbing potential at the interface, would not be expected to be screened rapidly in these materials with large gap and small dielectric constant. Although the individual wavefunctions themselves still have a strong superlattice character, most properties of interest are integrated properties, which are not sensitive to individual wavefunctions since all the bonding states are filled and the antibonding states are empty.

Although the band edges themselves are not well developed in a 5-layer/5-layer superlattice, it is nevertheless possible to obtain accurate values for the band edge discontinuities which, if they were to be obtained directly from the local density of states, would require considerably larger superlattices. Essentially, one makes use of the fact that the 1s core levels are close to their bulk value only 2-3 layers away from the interface. Calculations on bulk diamond and BN give the positions of the valence and conduction band edges relative to the 1s core eigenvalues; this information can then be used to place the band edges on either side of interface. A detailed discussion is given in [8].

The resulting band structure and lineups are shown in Fig. 1. The central result is that the (smaller) bandgap of diamond does not lie within the bandgap of BN, but rather a type-II alignment is obtained. The BN valence-band maximum is predicted to lie 1.42 eV below that of diamond, so holes at the interface will favor the diamond side. The conduction-band minimum of diamond lies higher than that of BN (by roughly 0.7 eV), so electrons at the interface will favor the BN side. This tendency toward charge separation at the interface may have useful applications in optoelectronic devices. Lambrecht and Segall [10] have obtained very similar results on the band lineups of this interface using different calculational methods.

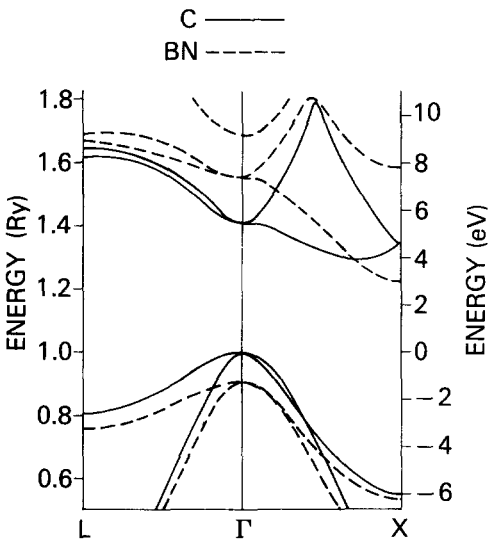

Figure 1. Lineup of the diamond and BN bands across the diamond/BN (110) interface. Note that a type-II alignment is obtained: at both the valence-band maximum and the conduction-band X point, the diamond bands lie above the BN bands. For the conduction bands at the zone center, the ordering is reversed.

Diamond/Ni Interfaces

Two of our primary aims in studying diamond/Ni interfaces have been (i) to gain insight into the mechanism behind formation of a Schottky barrier, and (ii) to make a quantitative prediction of the Schottky barrier height (SBH). The first issue is a long-standing problem in condensed-matter physics; a host of diverse experimental observations must be accounted for (pinned vs. non-pinned behavior of the Fermi level, pinning with respect to either the valence or conduction band, etc.), and a complete solution must address disordered as well as epitaxial interfaces, chemical bonding, strain due to lattice mismatch, intermixing, and so on. The second issue is more tractable: prediction of a *particular* SBH is "simply" a matter of knowing the structure and then calculating the energy spectrum. Unfortunately, there exists no experimental information whatsoever regarding the structure of the diamond/Ni interface; indeed, numerous efforts to grow such an interface epitaxially have been unsuccessful.

Without reliable structural information, one must either look for insight from chemical bonding arguments, or turn to computational total energy methods. We have tried to use a combination of these two approaches, in order first to reduce the vast number of structural possibilities to a manageable few, and second, to reliably identify the preferred (lowest energy) structures within that limited set.

As described in Sec. 2, two interface orientations were investigated. The first ("tetrahedral orientation")

maintains approximate tetrahedral coordination of the interface-layer C atoms; since Ni atoms are placed in line with C dangling bonds, we hoped that this orientation would not severely disrupt the C bonding near the interface. The second ("metallic orientation") places the Ni atoms in the hollows formed by surface-layer C atoms; by maintaining high coordination of the interface-layer Ni atoms, a structure is formed that is presumably favorable for metallic bonding. The two orientations lead to qualitatively different results for both the (100) and (111) interfaces.

For the (100) interface, the tetrahedral orientation places Ni atoms at a position, with respect to the C surface layer, known as the "bridge site". This calculation has been discussed previously [7], so here we summarize our results only briefly. For an assumed C-Ni inter-layer separation of 2.66 a.u. (roughly midway between the C-C and Ni-Ni inter-layer separations), our calculated SBH was very small or zero. The layer-projected DOS (LDOS) showed a C dangling-bond state localized at the interface C layer, centered at an energy roughly 2/3 of the diamond gap value. We interpreted this result as arising from a bonding mismatch between C and Ni, whose valence bands have very different widths (approximately 22 and 4 eV, respectively). Indeed, despite our strategy of maintaining tetrahedral coordination of the C atoms at the interface, the C-Ni bonding across the interface was minimal. We note, however, that a non-bonding or anti-bonding relationship between C and Ni layers does not *per se* imply a zero SBH. For this geometry, a small amount of charge transfer takes place, essentially restricted to the C and Ni interface layers and just sufficient to raise the Fermi level to the diamond VB maximum; this is a minimal consequence of satisfying the physical requirement of charge neutrality in the interior of the diamond slab. Without greater orbital overlap between the atoms at the interface layers, the interaction that is needed over a larger distance scale--in order to give a non-zero SBH--cannot arise.

At the (111) interface, the tetrahedral orientation places surface Ni atoms in the "atop" position, with respect to the C surface layer, again in line with the C dangling bonds. As we have discussed elsewhere [11], the results are qualitatively very similar to the (100) bridge-site orientation. For an assumed inter-layer

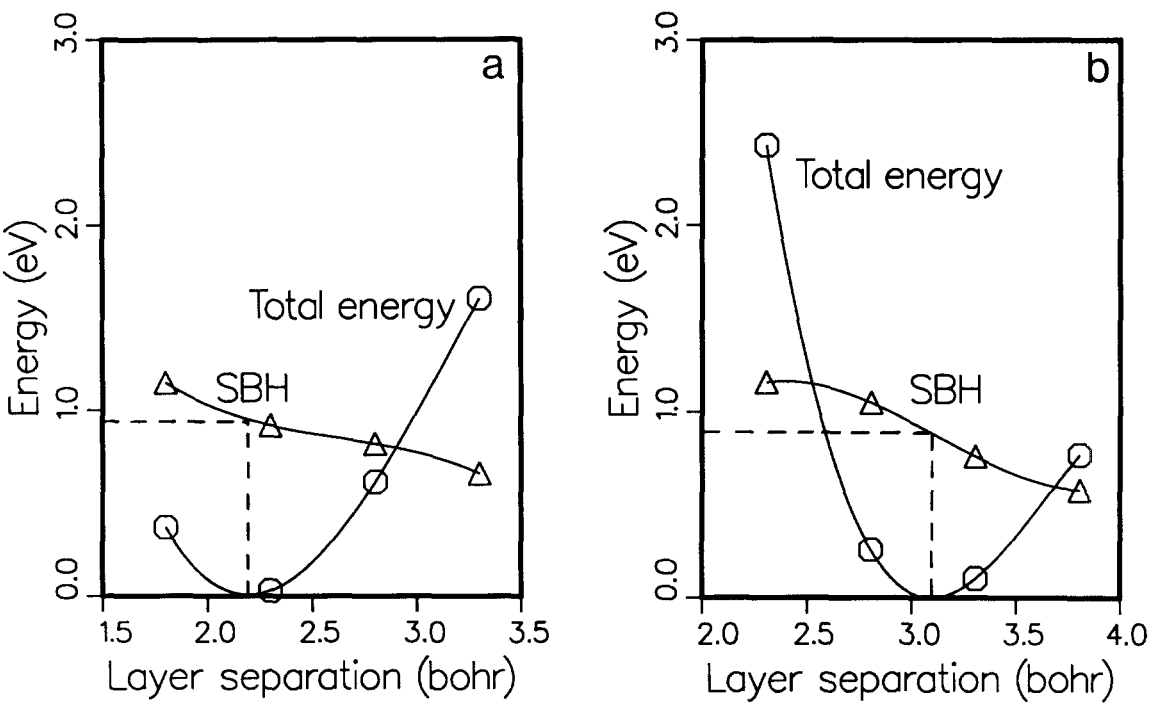

Figure 2. Total energies and Schottky barrier heights (SBH) for the diamond/Ni (001) and (111) interfaces, shown in (a) and (b), respectively. The "metallic" orientations of both interfaces are chosen so that Ni atoms sit in hollows formed by surface C atoms. Note that the SBH at the minimum energy separation (dotted line) is nearly the same for the two interfaces.

separation, the calculated SBH is again zero, and the LDOS reveals a similar dangling-bond-like feature in the diamond-gap region, also completely localized at the interface layer. In this case, the dangling-bond states fall in the *lower* 1/3 of the diamond gap, indicating somewhat more favorable bonding between C and Ni layers. This is born out by charge-density plots, which for this (111) orientation show a substantial charge accumulation along the axis formed by interface C and interface Ni atoms, with a peak value roughly half that of bulk diamond. However, the zero SBH supports the argument above, namely that this tetrahedral orientation does not provide sufficient wavefunction overlap to result in a non-zero SBH.

We turn now to the metallic orientations, which place surface Ni atoms in sites of high coordination. For the (100) interface, this site is a four-fold hollow; for the (111) interface, it is a three-fold hollow, known as the T_4 site with respect to the C surface. For both interfaces, we have varied the C-Ni interlayer separation to minimize the total energy, monitoring the SBH as a function of interlayer separation (Fig. 2). We find that at their minimum energy separations, the SBH's for the (100) and (111) interfaces are nearly equal, with a value close to 0.9 eV. By varying the inter-layer separation enough to raise the total energy above its minimum by 1 eV, the SBH changes by roughly 0.2-0.3 eV, indicating a weak-to-moderate dependence of the SBH on the total energy. On the other hand, the SBH is considerably more sensitive to variations in the C-Ni inter-atomic distance, with variations of 5% in the C-Ni atomic separation giving rise to variations of 10-20% in the SBH for both interfaces. We note that similar variations carried out for the tetrahedral orientations did not change the zero SBH result for that case. Thus, we tentatively conclude that while SBH's for these diamond/Ni interfaces are very sensitive to changes in interface orientation *parallel to the surface* (i.e. tetrahedral vs. metallic orientation), they are only moderately sensitive to changes in orientation *perpendicular* to the surface. This result is of more than theoretical interest, as it indicates the importance of growing an epitaxial, thermodynamically stable diamond/Ni interface. A disordered (or polycrystalline) interface would presumably show a Schottky barrier whose effective height is an weighted average of SBH's from numerous small epitaxial regions; regions far from

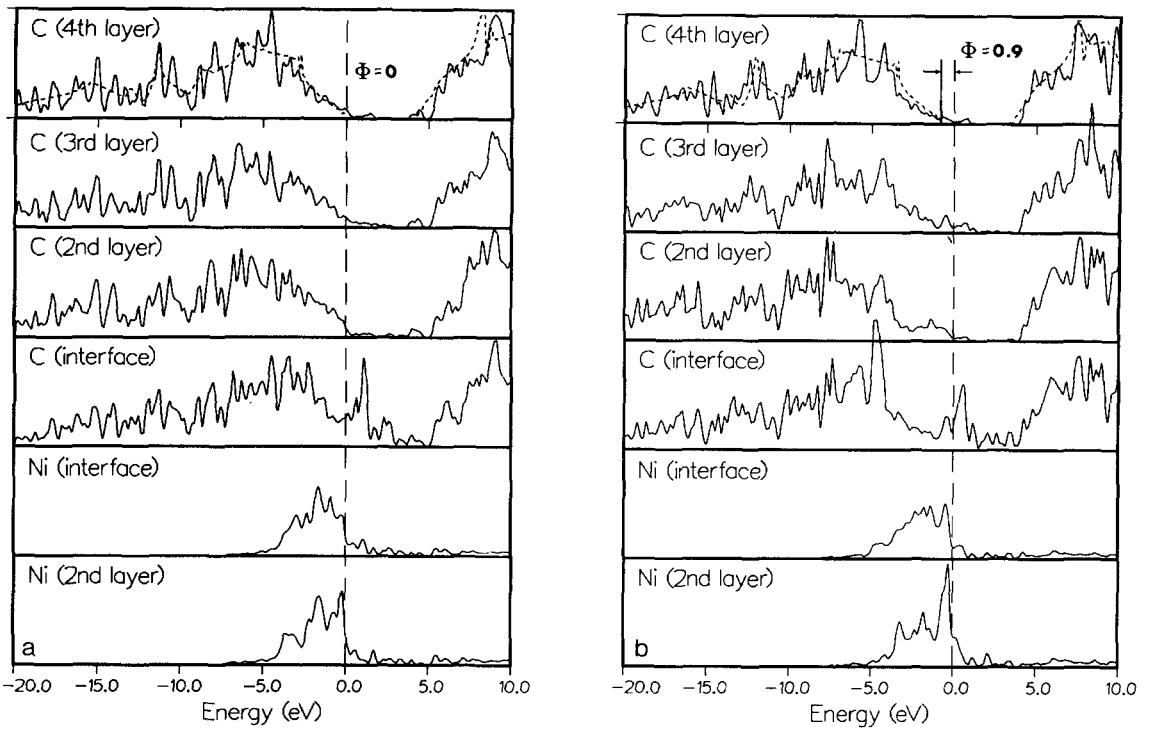

Figure 3. Layer-projected densities of states (LDOS) for the diamond/Ni (111) interface in the (a) tetrahedral (atop) and (b) metallic (T_4) orientations. For both orientations, a dangling-bond-like feature appears at the interface C layer. In the T_4 orientation, the disturbance of the C-layer LDOS penetrates further into the bulk, resulting in a Schottky barrier height of 0.9 eV.

the minimum-energy orientation will contribute only slightly (if at all) to the effective barrier height, thus reducing its value from the maximum value of 0.9 eV.

Finally, in Fig. 3a and 3b we show the LDOS for the (111) interface in the tetrahedral (atop) and metallic (T_4) orientations, respectively. As noted above, the atop orientation results in a dangling-bond-like feature in the lower 1/3 of the diamond gap, strongly localized at the interface layer. In the T_4 orientation, this feature has become somewhat broader, and has been pulled down to sit almost at the Fermi level. Furthermore, in the energy range -4 to 0 eV, the C-layer LDOS shows significant differences for the two orientations. For the atop orientation, the LDOS for the 2nd and 3rd C layers all already quite bulk-like, while for the T_4 orientation the LDOS in this energy range is somewhat flatter. For both orientations, there is clearly a large disruption of the bonding at the interface; while this disruption heals quickly for the atop orientation, it penetrates more deeply into the diamond bulk for the T_4. The longer range of interaction afforded by the metallic T_4 orientation is clearly a requirement for the formation of a non-zero SBH.

4. Summary

For the diamond/BN interface, our choice of atomic geometry at the (110) interface is very realistic, and the prediction of a type II band line-up, with a valence band offset of 1.42 eV, is probably accurate. For the diamond/Ni (100) and (111) interfaces, the Schottky barrier heights are strongly dependent on changes in interface orientation parallel to the interface (tetrahedral vs. metallic orientation), but only moderately dependent on changes perpendicular to the interface. For geometries near the total energy minimum, the Schottky barriers are pinned around 0.9 eV for both the (100) and (111) interfaces.

Due to the large cohesive forces in these materials, all have high surface energies, and hence are not easy to grow as the flat, high grade thin films that are easiest to study experimentally and to model theoretically. Nevertheless, for heterojunction formation, BN and Ni provide perhaps the most likely semiconducting and metallic candidates, respectively, and attempts to fabricate clean interfaces are continuing. Further theoretical understanding of both the diamond/BN and diamond/Ni interfaces will no doubt benefit greatly from the experimental information that we hope is forthcoming.

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